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SUMMARY OF NEW PESTICIDE ACTIVE INGREDIENT USE TRACKING FOR FIELD MONITORING IN SURFACE WATER FROM 2005-2010

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I. INTRODUCTION

The Department of Pesticide Regulation's (DPR's) Pesticide Registration Branch coordinates the registration process of new pesticide active ingredients (a.i.s) in California (CDPR, 2010). These pesticides are either already federally registered by the U.S. Environmental Protection Agency (USEPA) or under concurrent review by USEPA and DPR. New a.i.s are evaluated by several branches within DPR, including the Environmental Monitoring Branch (EMB). As part of the review process, EMB evaluates an a.i.'s potential for adverse effects to non-target aquatic organisms when used according to the product label. This is determined by assessing physical chemical properties, aquatic toxicity, runoff potential, and soil/sediment fate of the a.i.'s in surface water. EMB also decides whether potential risks can be mitigated with protective label language or other use restrictions.

During registration, future regional use intensity cannot be predicted but may be a major factor contributing to off-site movement (Spurlock, 2002). When EMB evaluates an a.i. for registration, attention is focused on the registrant's proposed uses of the products. Following initial evaluation and approval of an a.i., pesticide registrants may develop more products labeled for additional sites and crops, leading to increased use. Over time this additional use may lead to more frequent detections and aquatic toxicity problems, and the eventual need for monitoring, mitigation, or reevaluation of a pesticide or class of pesticides. One example of this effect of increased use is synthetic pyrethroids. These insecticides replaced many uses of organophosphate insecticides, with subsequent toxicity observed in surface water and sediment laboratory bioassays. For example, the use of the pyrethroid cypermethrin grew from 433 lbs in 1997 to 136,284 lbs in 2000 and 302,982 lbs in 2002 (CDPR, 2010). As a result of increased use and toxicity concerns all pyrethroids are currently in reevaluation in California by DPR (Cortez, 2006).

In an effort to better track newly registered pesticides the EMB is beginning an annual review of new a.i.s. with respect to increases of use and whether regional use presents risks to surrounding watersheds and warrants water quality monitoring.
There were 118 new a.i.s registered for use from 2005-2010. Some a.i.s, such as pheromones, vertebrate pest repellants, egg viability reducers etc., are omitted from consideration in this report because their use patterns are considered low risk to surface

water. Of the remaining 56 pesticides (Appendix 1), 12 exceeded 5,000 lb in use in a calendar year (Table 1), set as a level above which further evaluation is conducted (Newhart, 2011).

II. OBJECTIVE

In this study, DPR staff report 2005-2010 annual use, primary application sites, and aquatic toxicity data for all AIs registered since 2005 that meet the criteria for minimum use. That criterion is total statewide use > 5,000 lbs a.i. in at least one year since 2005. The compiled use and toxicity data are used to determine monitoring priorities for the new a.i.s.

Table 1. New active ingredients with use >5,000 lbs/year during 2005-2010 (CDPR, 2010).

Active Ingredient	Pesticide Type	Current Number of Active Products
Flonicamid	Insecticide	6
Aminopyralid triisopropanolamine salt	Herbicide	4
Propamocarb hydrochloride	Fungicide	5
Spinetoram	Insecticide	6
Spirodiclofen	Miticide	1
Flubendiamide	Insecticide	5
Spiromesifen	Insecticide	5
Mandipropamid	Fungicide	3
Chlorantraniliprole	Insecticide	13
Famoxadone	Fungicide	1
Metconazole	Fungicide	4
Penoxsulam	Herbicide	11

III. DATA SOURCES

Total statewide pesticide use and use by site data (Table 2; Figures 1 and 2) were obtained from the Department of Pesticide Regulation's Pesticide Use Reporting Database (CDPR, 2010).

Acute and chronic toxicity data for *Daphnia magna, Daphnia pulex, Hyallela azteca, Mysidopsis bahia, Onchoryncus mykiss, Lepomis macrochirus, and Selanastrum capricornutum* were obtained from registrant reports, the USEPA EcoTox Database (USEPA, 2011), USEPA evaluation reports, EUFootprint data (EUFootprint, 2011), and peer reviewed scientific articles.

Potential acute aquatic toxicity risk based on the seven species followed guidelines established by E. Zucker (1985), consisting of 5 classification categories (Table 3).

Table 2. Pounds active ingredient reported used from 2005-2010 (CDPR, 2010).

Active Ingredient	Year					
	2005	**2006**	**2007**	**2008**	**2009**	**2010**
Flonicamid	NR*	40	18,318	21,266	13,220	18,625
Aminopyralid triisopropanolamine salt	NR	73	6,544	11,440	16,995	24,073
Propamocarb hydrochloride	5	364	137,589	116,725	106,078	99,463
Spinetoram	NR	NR	362	20,074	25,018	26,028
Spirodiclofen	NR	4	28,864	32,369	44,850	30,580
Flubendiamide	NR	NR	NR	241	13,826	10,553
Spiromesifen	13,939	39,056	44,832	47,609	39,664	33,065
Mandipropamid	NR	NR	NR	5,428	15,199	25,196
Chlorantraniliprole	NR	NR	NR	10,459	25,539	37,766
Famoxadone	NR	6,563	3,831	3,109	3,514	9,013
Metconazole	NR	NR	NR	NR	4	15,939
Penoxsulam	NR	2,620	2,962	2,758	3,116	5,017

*NR- Not Registered

In addition to these general categories, chronic risk, bioaccumulation, and sediment effects were assessed as part of overall aquatic toxicity threat when individual species information are available. USEPA Level of Concern (LOC) and other aquatic benchmark information were obtained from USEPA reports when available. The critical value limit DPR staff is using for determining potential sediment risk is based on a soil adsorption coefficient KOC equal to or greater than 1000. Values <1000 are considered more likely to move off-site in surface water because the a.i. does not attach itself to soil particles and has low sediment bioavailability. In contrast, when KOC is >1000, the a.i. attaches to soil particles or organic matter and has a greater potential for sediment toxicity. The KOC cut-off of 1000 is the USEPA threshold for submission of sediment toxicity data for new active ingredients, but not an official cut-off value for sediment risk assessment (USEPA, 2007(a)). DPR uses that threshold for evaluation because chemicals with lower KOC values usually have no reported sediment toxicity.

Table 3. USEPA classification (Zucker, 1985) of toxicity categories and toxicity ranges.

LC_{50} (EC_{50}) ppm	**Category Description**
<0.1	Very highly toxic
0.1-1.0	Highly toxic
>1.0 < 10.0	Moderately toxic
>10.0 <100	Slightly toxic
>100	Practically non-toxic

Figure 1. New pesticide active ingredient (a.i) by pounds and year applied from 2005-2010.

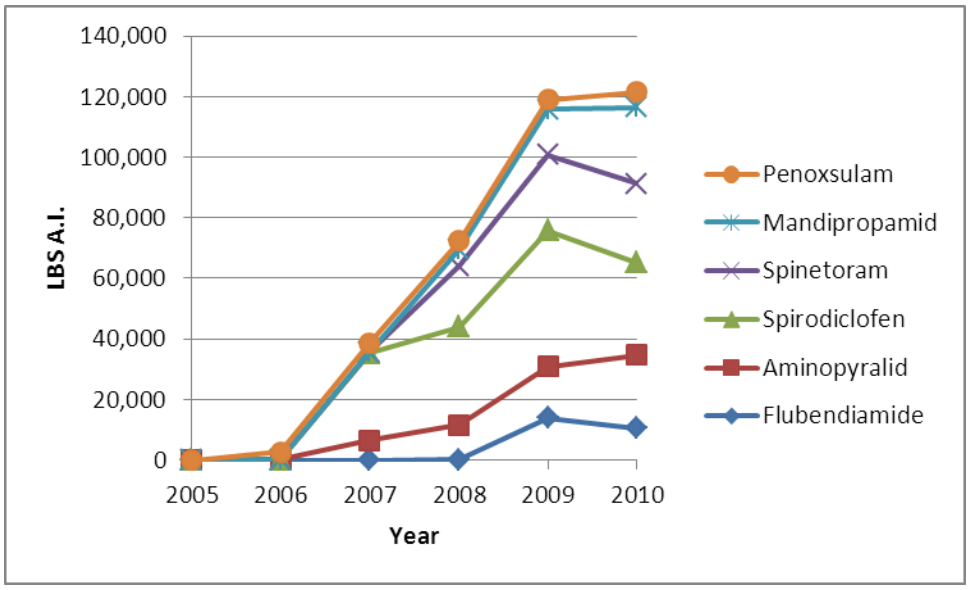
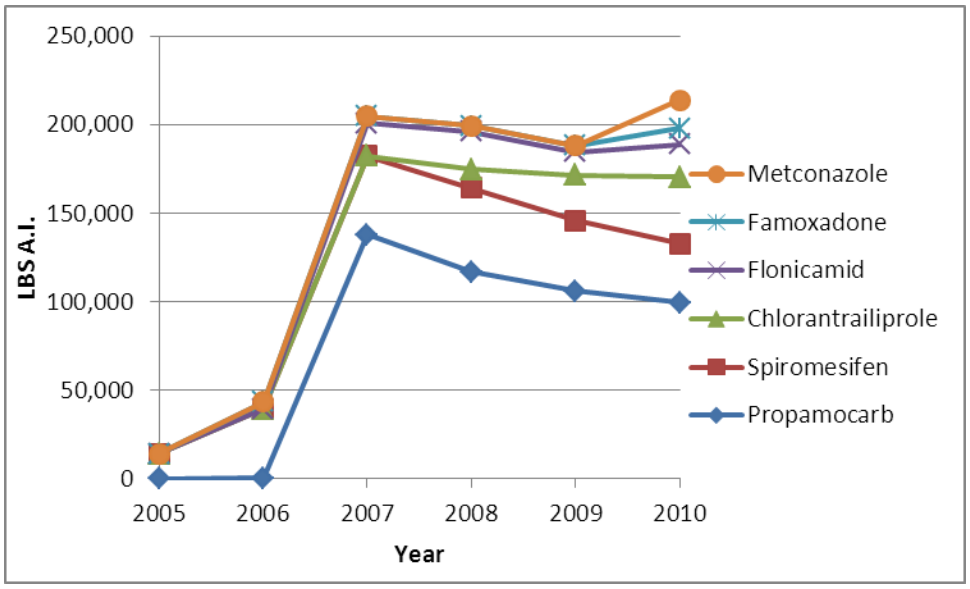


Figure 2. New pesticide active ingredient (a.i) by pounds and year applied from 2005-2010.



IV. RESULTS

The following are summaries of a.i.s from 2005-2010 selected for further assessment (Table 2). Descriptions of each a.i. and its chemical characteristics, uses, and toxicities to aquatic organisms are summarized in Table 4.

Propamocarb

Propamocarb was initially registered for various field crops in 2005. Currently there are five active products registered in California (CDPR, 2010). A product labeled for ornamental and nursery uses was added in 2007. Three new products were added in 2009 with one specific to lettuce crops, one for additional ornamentals and one for turf. Propamocarb hydrochloride had the highest use of all of the a.i.s summarized from 2005-2010, with 99,456 lbs a.i. applied in 2010. Use (a.i.) was the highest in 2007 (137,589 lbs), followed by 2008 (116,725 lbs), and 2009 (106,078 lbs). Lettuce was the main site of propamocarb use in Fresno, Imperial, Monterey, Riverside, San Benito, San Luis Obispo, Santa Barbara, Santa Clara, Santa Cruz, and Ventura counties (CDPR, 2010). In 2010, 90,062 lbs a.i. was applied to 89,762 acres of lettuce crops (CDPR, 2010).

Propamocarb is "practically non-toxic" to aquatic species based on the criteria of Zucker (Table 3), with LC50 values >106 mg/L for fish species and *Daphnia magna* (Shelgren, 2002, EUFootprint, 2011). The KOC of propamocarb is 535 and has a water-sediment DT50 of 17 days making it unlikely to accumulate in sediment. USEPA determined that propamocarb "dissipates rapidly in field conditions and has variable mobility from mobile-relatively immobile" depending on soil conditions (USEPA, 1995).

Propamocarb use is not concentrated in a single geographic area to a degree that would constitute a current regional problem in California (CDPR, 2010). DPR staff recommends that propamocarb requires no further tracking at this time due to its low potential for runoff and aquatic toxicity.

Chlorantraniliprole

Chlorantraniliprole is an anthranilic diamide insecticide and use has increased from 10,459 lbs a.i. in 2008 to 37,775 lbs a.i. in 2010 (CDPR, 2010). There are currently 13 active products registered in California. Chlorantraniliprole is labeled for use on a wide variety of use sites and targets numerous pests, making it an a.i. for potential future monitoring based on possible increases of use, runoff potential to surface water, and toxicity to aquatic species (Newhart, 2008).

The largest use of chlorantraniliprole in 2010 was on almonds (8,531 lbs a.i. on 106, 204 acres) in Kern and Madera counties. The next highest use was on wine grapes (4,664 lbs a.i.) applied to 55,136 acres. Napa County reported 2,810 lbs a.i. applied to 29,955 acres on wine grapes. Walnuts were treated with 2,704 lbs a.i. applied to 32,527 acres, and peaches were treated with 1,791 lbs a.i. applied on 21,126 acres. The remaining

applications were spread out between structural pest control, landscape, nursery container plants, berries, citrus, pistachio, apples, pears, apricot, cherries, nectarines, plums, prune, melons, pomegranate, cucumbers, squash, peppers, eggplant, tomatoes, broccoli, various cole crops, spinach, and lettuce. Chlorantraniliprole use amounted to < 100 to a few hundred lbs. of a.i. in these scenarios.

Chlorantraniliprole has a KOC of 328, is considered persistent and mobile in surface water and displays relatively high aquatic toxicity (Bireley and Lopez, 2008; USEPA, 2007b). It has a soil degradation half-life of 181-222 days when applied at 0.286 lbs a.i./acre for dissipation studies conducted in California and Texas, and can accumulate due to carry over in soil year-to-year (USEPA, 2008). The aerobic aquatic metabolism for chlorantraniliprole is 231 days and hydrolytic half-life is >30 days. The water/sediment photolysis half-lives were 0.31 and 0.37 days in sediment free water (USEPA, 2007b, MRID 46889018). In a water/sediment system chlorantraniliprole had photodegradation half-lives of 22 days in loamy sand sediment and 9.9 days in a sandy loam sediment system (USEPA, 2007b, MRID 46889122). In another study chlorantraniliprole persisted (half-life =231 and 125 days) under stratified redox test conditions in sand and loam sediment water systems (USEPA, 2007b, MRID 46889016).

Aquatic toxicity of chlorantraniliprole has been extensively reviewed and summarized as part of the conditional registration for new proposed product registrations in California (Newhart, 2008). The 48-h LC50 for *Daphnia magna* (water flea) was estimated at 0.0116 ppm (very highly toxic), 1.15 ppm for *Mysidopsis bahia* (Mysid Shrimp) (96-h LC50) (moderately toxic), 0.389 ppm (48-h LC50) for *Hyalella azteca* (amphipod) (highly toxic), 0.0859 for *Chironomus raparius* ((Midge) 48-h LC50) (very highly toxic), and 13.8 ppm (48-h LC50) for *Onchorynchus mykiss* (rainbow trout) (slightly toxic) (Bireley and Lopez, 2008).

DPR staff recommends that chlorantraniliprole be considered for further detailed analysis of use pattern and toxicity data to determine whether monitoring is warranted. This determination is based on its increase in use, high aquatic toxicity, and runoff potential.

Spiromesifen

Spiromesifen is an insecticide with a wide variety of ornamental and crop uses. There are five active products registered in California. The highest use was on corn (22,910 lbs a.i.) in 2010. Targeted pests include mites/ticks, red spiders, leaf hoppers, psyllids, whitefly, and scale insects. Use of spiromesifen totaled 33,065 lbs a.i. in 2010. Application sites included landscape/greenhouse (<500 lbs a.i.), outdoor ornamental (<58 lbs a.i.), strawberry (7,063 lbs a.i.), melons (977 lbs a.i.), squash (<20 lbs), peppers (534 lbs), tomatoes (217 lbs), corn (22,910 lbs), and cotton (934 lbs) (CDPR, 2010).

EUFootprint classifies spiromesifen as moderately persistent based on an aqueous hydrolysis DT50 of 44.7 days. Degradation of spiromesifen in water-sediment systems is fast with a DT50 of 4-11days (Shelgren, 2003). The water phase only DT50 is also fast at 0.15 days. Spiromesifen has a KOC of 30,900 (EUFootprint, 2011). Soil degradation is

considered non-persistent with a field soil DT50 of 9 to 14 days (Shelgren, 2003).The KOC of spiromesifen is >31,000 and it binds readily to soil (Shelgren, 2003).

Aquatic toxicity for *Onchorhynchus mykiss* (rainbow trout) has an acute 96-h LC50 of 0.015 mg/L (very highly toxic) (EUFootprint, 2011). Spiromesifen is also considered very highly toxic to *Daphnia magna* (water flea) with an acute 48-h LC50 of 0.092 mg/L (Shelgren, 2003) and a chronic 21-d NOEC of 0.00025 mg/L (EUFootprint). Table 4 contains a summary of spiromesifen toxicity for additional organisms (Shelgren, 2003, EUFootprint, 2011).

DPR staff will continue to track the use of spiromesifen due to high potential for aquatic organism toxicity.

Spirodiclofen

Spirodiclofen has the next highest use of the new a.i.s with 30,589 lbs a.i. used in 2010 (CDPR, 2010). There is currently one active product registered in California. Spirodiclofen is a selective, non-systemic miticide mostly used on orchard trees (almonds, peach, walnut, nectarines, plum, cherry, citrus) and wine grapes (CDPR, 2010). The main use is in the San Joaquin Valley including Fresno, Kern, Kings, San Joaquin, Stanislaus, Madera, and Tulare counties (CDPR, 2010). Highest use was on almonds (11,603 lbs a.i.) and stonefruit (5,828 lbs a.i.) in 2010. Other crops spirodiclofen was applied in 2010 were citrus (5,243 lbs a.i.), walnuts (3,651 lbs a.i.), and grapes (3,864 lbs a.i.). The remaining crops and sites include rights-of-ways, container plants, pistachio, apples, and pears and account for the remaining 5,996 lbs a.i. applied.

Spirodiclofen is considered very highly toxic to rainbow trout (*Onchorynchus mykiss*) with a 96-h LC50 of 0.0351 mg/L, *Daphnia magna* (water flea) (48-h EC50- 0.05 mg/L), and *Chironomous riparius* (midge) (96-h LC50-0.032 mg/L) (Shelgren, 2006d). The aquatic half-life is short for spirodiclofen at <1 hour-4 days. Breakdown products are considered persistent and are more mobile than the parent chemical. The KOC range is 31,037 to 238,000 for parent spirodiclofen making it immobile in soil (USEPA, 2005). Spirodiclofen has low water solubility (50µg/L), hydrophobicity, and tends to bind to soil and sediment and bioconcentrate in aquatic species (USEPA, 2005).

Spirodiclofen dissipates rapidly by photolysis in water with a half-life of <1 hour-4 days (USEPA, 2005). Field dissipation studies conducted in California, Florida, Washington, and Canada yielded 3-5 day half-lives (USEPA, 2005). Estimated surface water environmental concentrations (EECs) for spirodiclofen were calculated by USEPA with PRZM/EXAMS for six different crops and concentrations ranged from <1 ppb to approximately 4 ppb. Spirodiclofen has a1-7 day dissipation in water/sediment aerobic conditions and approximately 40 days in anaerobic aquatic systems (USEPA, 2005).

DPR staff recommends that spirodiclofen use be further tracked due to its high risk potential for aquatic toxicity.

Spinetoram

Spinetoram statewide use in 2010 was 26,028 lbs a.i. (CDPR, 2011). There are six active products registered in California. Spinetoram is a synthetic insecticide that acts on nicotinic receptors and mostly targets Thysanoptera, Coleoptera, Diptera, and Lepidopteran insects on wide range of field crops. Methods of application include ground, aerial, and direct soil applications.

The highest use of spinetoram in 2010 was on lettuce (4,010 lbs a.i.), citrus (3,614 lbs a.i.), berries (2,963 lbs a.i.), grapes (2,480 lbs a.i.), and 1,835 lbs a.i. on stone fruit. Other crops that accounted for remaining uses included celery, various herbs, leeks and onions, endive, cauliflower, Chinese cabbage, tomatoes, peppers, corn, turnips, peas, mustard, and others.

Aqueous hydrolysis for spinetoram is considered stable and highly persistent (EUFootprint, 2011). The KOC is 22,836 and makes it non-mobile (EUFootprint, 2011). It has a half-life in soil (field) of 4.5 days and is considered non-persistent (EUFootprint, 2011). Spinetoram is a fermentation product of *Saccharopolyspora spinosa*, an analogue of and considered toxicologically identical to spinosad (USEPA, 2009). Metabolites are considered to be toxicological equivalents to the parent (USEPA, 2009) with relative low solubility in water (20 mg/L spinetoram, and have an affinity for binding to organic carbon in sediment and suspended solids (USEPA, 2009).

Spinetoram is highly toxic (0.355 mg/L) to *Americamysis bahia* (mysid shrimp) and to *Crassostrea virginica* (eastern oyster) (0.393 mg/L) (Shelgren, 2006c). USEPA determined the largest toxic risk exists to freshwater invertebrates on reproduction, growth, and decreased survival from the use of spinetoram. Additional toxic risks exist to freshwater benthic invertebrates (chronic) and aquatic non-vascular plants (USEPA, 2009). Chronic risks to benthic invertebrates exist to reduced emergence and development (USEPA, 2009).

DPR staff will continue tracking spinetoram use due to its high aquatic toxicity and nature to bind to sediment.

Mandipropamid

Mandipropamid is a fungicide in the mandelamide chemical class, and is applied to a wide variety of field crops and grapes. Three products are currently registered in California. Highest yearly use of mandipropamid was 25,230 lbs a.i. in 2010 (CDPR, 2010). Mandipropamid is labeled to treat *Plasmopara viticola* (grapevine downy mildew) in grape, *Phytophthora infestans* (late, early blight) in potatoes and tomatoes, *Pseudoperonospora cubensis* (cucurbit downy mildew) in cucurbits, *Bremia lacucae* (downy mildew) and *Peronospora effuse* (blue mold) in leafy vegetables. It can be applied as a post-emergence foliar spray, ground or aerial, or chemigation treatment.

The highest use of mandipropamid in 2010 was on lettuce crops (18,714 lbs a.i.) and spinach (3,837 lbs a.i.). Other crops that were treated included cabbage, kale, endive, collard, cauliflower, Swiss chard, arugula, fennel, mustard, tomatoes, onions, and potatoes. Other relatively minor use was on ornamentals and landscape maintenance.

The water solubility is 4.2 mg/L with a photolysis half-life of 0.63-1.1 days in pH 7.0 at 25^{o}C. The soil photolysis half-life is estimated at 16.4-23.9 days (USEPA, 2008). Mandipropamid has multiple breakdown products that rapidly degrade to non-extractable residues and carbon dioxide (USEPA, 2008). The aerobic aquatic half-life was found to be 17.8-18.5 days in river water/silt loam sediment systems in England and Germany (USEPA, 2008). In California a sandy loam field plot planted with field potatoes was found to have a half-life of mandipropamid of 75.3 days in a field dissipation study (USEPA, 2008).

Mandipropamid can be a "runoff risk for months following application" (Syngenta, 2011) and is relatively stable to aqueous hydrolysis (very persistent) (EUFootprint, 2011). Mandipropamid has a relatively low water solubility of 4.2 mg/L (20^{o}C). It has a water/sediment DT50 of 12.2 days. Mandipropamid has a DT50 of 13.6 and DT90 of 76.4 days in aerobic soil field conditions (EUFootprint, 2011).

Toxicity of mandipropamid is listed in Table 4. The most sensitive species listed is *Crassostrea virginica* (eastern oyster) with a 96-h acute EC50 of 0.97mg/L (highly toxic) (Shelgren, 2007a). Other species are listed as moderately toxic and include *Lemna gibba* (duckweed) with an acute 7-d EC50 of >4.4, biomass (mg/l) (EUFootprint, 2010), *Daphnia magna* (water flea) of 7.1mg/L (acute 48-h EC50) (EUFootprint), and *Americamysis bahia* (mysid shrimp) with a 96-h LC50 of 1.7mg/L (Shelgren, 2007).

DPR staff recommends mandipropamid use will be further tracked due to its high aquatic toxicity and nature to remain a runoff risk for months following application.

Aminopyralid

Aminopyralid is labeled for use on many agricultural crops, ornamental, and landscape maintenance sites, and currently four products are registered in California (CDPR, 2011). Aminopyralid's highest use occurred in 2010 with 24,073 lbs a.i. reported applied (CDPR, 2011). The sites with the highest use were rights-of-way (20,912 lbs a.i.), landscape maintenance (1,150 lbs a.i.), regulatory (1,313 lbs a.i.) and pasture/rangeland (1,177 lbs a.i.) (CDPR, 2011).

A pyridine carboxylic acid herbicide aminopyralid has high solubility in water (2,480 mg/L) and is stable and very persistent to aqueous hydrolysis (EUFootprint, 2010). The main route of degradation for aminopyralid is by aqueous photolysis (fast) with a DT50 of 0.6 days (EUFootprint, 2011). Aminopyralid is considered very persistent and has a water phase DT50 of 250 days and a water-sediment DT50 of 712 days (EUFootprint, 2011). Aminopyralid is very mobile with a KOC of 8.3 and is considered non-persistent in field soil with a DT50 of 21.1 days (EUFootprint, 2011).

Aquatic toxicity is slightly to practically nontoxic based on acute 96-h LC50s of 100 mg/L for *Americamysis bahia* (mysid shrimp) and >100 mg/L for *Onchorynchus mykiss* (rainbow trout) (EUFootprint, 2011, Shelgren, 2006b). *Daphnia magna* (waterflea) has an acute 48-h EC50 of 98.6 mg/L to aminopyralid (Shelgren, 2006b).

DPR staff will continue to track aminopyralid use due to its persistence and surface water runoff risk.

Flonicamid

Flonicamid is a systemic insecticide with long term activity. There are six active products labeled for use on many various field crops and ornamentals in California. The highest year of use of flonicamid occurred in 2008 with 21,266 lbs a.i. applied (CDPR, 2010). There were 18,392 lbs a.i. applied in 2010 with the largest use on cotton with 14,852 lbs, followed by alfalfa (891 lbs), and lettuce (817 lbs a.i.) (CDPR, 2010).

Flonicamid has high water solubility (5,200 mg/L), is stable to aqueous photolysis, and is stable/very persistent to aqueous hydrolysis (EUFootprint, 2011). The water phase DT50 is 33.8 days (stable) and the water-sediment DT50 is 40 days (moderately fast) (EUFootprint, 2011). Flonicamid is non-persistent in soil with a DT50 of 3.1 days. The low KOC of 5.9 implies very high mobility and very low affinity for soils and sediment (EUFootprint, 2011).

Flonicamid has an acute 96-h LC50 of >100 mg/L (practically non-toxic) for *Oncorhynchus mykiss* (rainbow trout) and >128 mg/L *Lepomis macrochirus* (bluegill sunfish) (EUFootprint, 2011, Shelgren, 2006a).

Based on these data, flonicamid has relatively low potential for aquatic toxicity in the environment. DPR will continue to track flonicamid use due to high mobility.

Flubendiamide

Flubendiamide is a benzene-dicarboxamide insecticide (EUFootprint, 2011) with a wide variety of crop, ornamental, and orchard uses. Five products are registered in California (CDPR, 2011). The highest use was in 2009 (13,826 lbs a.i.) and 2010 (11,902 lbs a.i.) reported applied. The most use in 2010 was on almonds (6,000 lbs a.i.), grapes (1,047 lbs. a.i), tomatoes (930 lbs. a.i.) and stone fruits (898 lbs. a.i.) (CDPR, 2011).

Flubendiamide solubility in water is low (0.029 mg/L) and it has a KOC of 2,197 making it only slightly mobile (EUFootprint, 2011). It is very highly toxic to *Daphnia magna* (waterflea) with an acute 48-h EC50 of 0.06 mg/L (Shelgren, 2007b). It is also very highly toxic to *Chironomus riparius* (midge) with an LC50 of 0.028 mg/L (Shelgren, 2007b), *Onchorynchus mykiss* (rainbow trout) with an acute 96-h LC50 of 0.0619 mg/L, and *Cyprinodon variegatus* (sheepshead minnow) LC50 of 0.0298 mg/L (Shelgren, 2007b).

DPR will continue to track flubendiamide due to high toxicity to aquatic species.

Famoxadone

Famoxadone is a synthetic oxazolidinedione fungicide with residual activity used to control downy mildew and blights (EUFootprint, 2011). Famoxadone is labeled for use on vegetable and row crops with the highest use on tomatoes, lettuce and cucumbers based on 2010 pesticide use reporting (CDPR, 2011). The year with highest use of famoxadone was 2010 with 9,013 total lbs active ingredient applied. The highest crop uses in 2010 were for head lettuce (1,533 lbs a.i.) and tomatoes (1,484 lbs a.i.).

Famoxadone has low solubility in water (0.11 mg/L), slight mobility, and fast breakdown in water with a hydrolysis half-life of 2 days at pH 7.0. The averaged KOC of famoxadone is 3,740 mL/g (Ratto, 2004). In the water-sediment phase famoxadone DT50 is from 0.68-2.1 (Ratto, 2004). Famoxadone is non-persistent in soil with a field degradation of 20 days (EU Footprint, 2011). A field dissipation study performed in California silty clay loam of famoxadone applied at 1.5 lbs/acre yielded a field half-life of 11days and is considered non-persistent (Ratto, 2004).

Famoxadone is very highly toxic to bluegill sunfish (0.013 mg/L), rainbow trout (0.011 mg/L), sheepshead minnow (0.0494 mg/L), Mysid shrimp (0.0390 mg/L), *Daphnia magna* (0.012 mg/L) (Shelgren, 2004a).

DPR will track the use of famoxadone due to high toxicity to aquatic species.

Metconazole

Metconazole is a triazole fungicide used to treat a wide range of fungal infections. There are four registered products with metconazole. Highest use in 2010 was on nut crops with 12,655 lbs a.i. applied to almonds and pistachios (CDPR, 2010). Other sites include landscape maintenance, stone fruits, wheat crops, turf/sod, and greenhouse/container plants.

Metconazole is very persistent and stable in aquatic sediments (DT50-465 days) and in-field DT50 is 265 days (Kelley, 2009). The KOC is 1294 giving it potential to adsorb to soil (Kelley, 2009). Metconazole has a high risk to move off-site in sediment (Kelley, 2009). Metconazole is stable in water slow hydrolysis and photolysis (DT50-36 days) (EUFootprint, 2011; Kelley, 2009). Metconazole has the potential to carry-over from successive seasons due to long half-lives in soil and sediment (Kelley, 2009).

The 96-h LC50s for aquatic organisms include 0.75 mg/L for Mysid shrimp (highly toxic) (Shelgren, 2009). Other toxicity values were in the "slightly toxic" category (Table 3) and include 3.9 mg/L for fathead minnow, 2.2 mg/L for Rainbow trout, and 6.3 for sheephead minnow (Shelgren, 2009). The 96-h EC50 is 2.3 mg/L (slightly toxic) for Eastern oyster (Shelgren, 2009; Table 4).

Metconazole will be on further tracking and possible monitoring based on soil and sediment accumulation concerns; although it is slightly toxic to aquatic organisms.

Penoxsulam

Penoxsulam is a triazopyrimidine sulfonamide herbicide (EUFootprint, 2011). There are 11 active products currently registered in California (CDPR, 2012). Since penoxsulam was registered for use in 2005 the highest use has been on rice with 2,500 lbs a.i. applied to rice in 2010 (CDPR, 2010). Other minor use is on nut crops, landscape maintenance, and rights-of-ways from 2006-2010.

Penoxsulam has a hydrolysis DT50 of 11-34 days, soil degradation DT50 of 32-46 days, and a water-sediment DT50 of 23 days (average) (Newhart, 2009). Penoxsulam is moderately soluble in water with a value of 408 mg/L (EUFootprint, 2010). It degrades quickly to levels well below aquatic toxicity values of sensitive species (Ma, 2008; Newhart, 2005). The KOC of penoxsulam is listed as 12-1141 mL/g and is considered moderately mobile (EUFootprint, 2010).

Penoxsulam degrades quickly in water by photolysis with a water phase half-life of 4.4 days. The degradation is slower in soil + water half-life of 6.5 days but does not pose hazard for accumulating in sediment (Shelgren, 2004b).

The 96-h LC50 for bluegill sunfish is >103 mg/L, 102 mg/L for rainbow trout, >114 mg/L for Mysid shrimp, and 98.3 mg/L for *Daphnia magna* (Shelgren, 2004b). The most sensitive aquatic species are duckweed (0.003 mg/L) and blue-green algae (0.49 mg/L) (EUFootprint, 2010). Penoxsulam has been extensively reviewed by CDPR staff and conclusions were that it poses little environmental risk to aquatic species.

Penoxsulam will not be tracked further based on low toxicity to aquatic species.

Criteria Ranking

Based on the analyses above, Table 4 summarizes the need for future recommended tracking and/or monitoring. The active ingredients are classified into one of three categories based on use, aquatic toxicity, surface water run-off potential, and likelihood for sediment accumulation:

A. No further tracking necessary
B. Watch List- no current monitoring but continued tracking necessary
C. Further detailed analysis of use pattern/toxicity data to determine whether monitoring is warranted.

DPR staff will continue to observe use changes of pesticides identified in the B and C categories due to their potential toxicity, runoff, or sediment accumulation risks.

Table 4. Summary table of results and recommendation for future actions.

Active Ingredient	Highest annual use (lbs a.i.)	Primary crops	Aquatic toxicity* mg/L	SummaryObservations	Status** A, B, C
Flonicamid	**21,266**	**Cotton, alfalfa, lettuce**	**Practically non-toxic >100**	• **Low current use** • **Low toxicity** • **High runoff risk** • **KOC>1000**	**B**
Aminopyralid triisopropanolamine salt	**24,073**	**Rights-of-way, landscape mnt., regulatory, rangeland**	**Practically non-toxic >100**	• **Low current use** • **Low toxicity** • **High runoff risk** • **KOC<1000**	**B**
Chlorantraniliprole	**37,766**	**Wine grapes, nut crops (walnut, almond), stone fruits, various row crops**	**Very highly toxic <0.1**	• **Use increasing** • **High Toxicity** • **High runoff risk** • **Accumulates in soil**	**C**
Propamocarb hydrochloride	**137.589**	**Lettuce, minor row crops**	**Practically non-toxic >100**	• **Low runoff potential** • **Low toxicity** • **High use** • **KOC<1000**	**A**
Spinetoram	**26,028**	**Lettuce, citrus, berries, grapes, stone fruit, various minor crops**	**Highly toxic 0.1-1.0**	• **Low current use** • **High Toxicity** • **Low runoff** • **KOC>1000**	**B**
Spirodiclofen	**44,850**	**Almonds, stone fruits, walnuts, pistachios, citrus, wine grapes**	**Very highly toxic <0.1**	• **Low current use** • **High Toxicity** • **Low runoff** • **KOC>1000**	**B**
Flubendiamide	**13,826**	**Almonds, corn, walnuts, various row crops**	**Very highly toxic <0.1**	• **Low current use** • **High toxicity** • **Slightly mobile** • **KOC>1000**	**B**
Spiromesifen	**47,609**	**Corn, peppers, greenhouse, various row crops**	**Very highly toxic <0.1**	• **Low current use** • **High toxicity** • **Low mobility** • **KOC>1000**	**B**
Mandipropamid	**25,196**	**Lettuce, leafy greens, minor row crops, various row crops**	**Very highly toxic <0.1**	• **Low current use** • **High toxicity** • **High runoff** • **KOC-405-1294**	**B**
Famoxadone	**9,013**	**Lettuce, tomato, various row crops**	**Very highly toxic <0.1**	• **Low current use** • **High toxicity** • **Slight run-off potential** • **KOC>1000**	**B**
Metconazole	**15,939**	**Nuts, stone fruits, landscape mtn.**	**Very highly toxic <0.1**	• **Increasing use** • **Slightly toxic but accumulates** • **Mobility and sediment risk** • **KOC>1000**	**B**
Penoxsulam	**5,017**	**Rice, nuts, landscape mtn.**	**Slightly toxic**	• **Low current use** • **Slightly toxic** • **Low runoff risk** • **KOC>12-1141**	**A**

*Toxicity determination based on reported values for most sensitive species. The aquatic species and their toxicities aresummarized in this report on sections discussing individual active ingredients.

**A. No further tracking necessary

B. Watch List- no current monitoring but continued tracking necessary

C. Further detailed analysis of use pattern/toxicity data to determine whether monitoring is warranted.

	Active Ingredients and Concentration (mg/L)											
Aquatic Species	**Flonicamid**	**Aminopyralid**	**Propamocarb**	**Spinetoram**	**Spirodiclofen**	**Flubendiamide**	**Spiromesifen**	**Mandipropamid**	**Chlorantraniliprole**	**Famoxadone**	**Metconazole**	**Penoxsulam**
***L. macrochirus* bluegill sunfish** (acute 96-h LC50)	100 [1]	>100 [4]	>95[5]	2.69 [6]	>0.045 [7]	>0.067 [8]	>0.0337 [9]		15.1 [11]	0.013[12]		>103[14]
***C.carpio* carp** (acute 96-h LC50)	70.6 [1]					>0.0847 [8]						101[15]
***O. mykiss* rainbow trout** (acute 96-h LC50)	>100 [3]	>100 [2,4]	>99 [2,5]	3.46 [3,6]	0.0351 [7]	>0.0619 [8]	>0.015 [9]	4.4 [10]	13.8 [11]	0.011[12]	2.2[13]	>102[15]
***C. variegatus* Sheepshead** (acute 96-h LC 50)	120 [2]	>120 [4]	>98.6 [3]		0.0352 [7]	>0.0298 [8]	>0.0463 [9]	4.5 [10]	12.0 [11]	.0494[12]	6.3[13]	
***A.bahia* mysid** (acute 96-h LC 50)	121 [2]	>100 [4]	104.7 [3]	0.355 [6]	.037 [7]	>0.028 [8]	>0.076 [9]	1.7 [10]	1.15 [11]	.00390[12]	0.75[13]	>114[15]
D. magna (acute 48-h EC50)	>100 [3]	>100 [1]	106 [5]	3.17 [6]	0.05 [7]	0.06 [8]	>0.0923 [9] (48-h LC50)	7.1 [10]	0.0116 [11]	0.012[12]	4.2[13]	>98.3[15]
***L. gibba* duckweed** (acute 7-d EC50)	119 [3]	88 [4]		14.2 [3]		0.0546 [3]	0.101 [3]	>4.4 [3]	2.0 [3]	0.081 (7d-EC50)[3]	>0.17[14]	.003[3]
***H. azteca* amphipod** (acute 48-h LC50)									0.389 [11]			
***P. subcapitata* algae** (acute 72-h EC 50)	>100 [3]	30 [4]			>0.06 [3]	0.069 [2]	>0.094 [3]		2.0 [11]		1.7[14]	
***C. riparius* midge** (acute 96-h LC50)		130[3] (28-d NOEC)		0.000375[3] (28-d NOEC)	0.032 [3]	0.825 [3]	0.1[3] (28-d NOEC)		0.0859[11] (48-h LC50)		2.12[14]	
***C. virginica* Eastern Oyster** (acute 96-h LC50)	128 [3]	>89 [4]	43.9 [5]	0.393[6] (96-h EC50)	>0.43 [7]	>.049[8] (96-h EC50)	>0.026 [9]	0.97[10] (96-h EC50)	39.9 [11]		2.3[13] (96h EC50)	>127[15] (96-h EC50)

[1]FMC MSDS, 2009
[2]Shelgren, 2006a
[3]EUFootprint, 2011
[4]Shelgren, 2006b
[5]Shelgren, 2002
[6]Shelgren, 2006c
[7]Shelgren, 2006d
[8]Shelgren, 2007
[9]Shelgren, 2003
[10]Shelgren, 2007
[11]Bireley and Lopez, 2008
[12]Shelgren, 2004a
[13]Shelgren, 2009
[14]Kelley, 2009
[15]Shelgren, 2004b.

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Appendix 1. Active ingredients registered by the Department of Pesticide Regulation from 2005 through 2010.

2005			
A.I. Registered	**Pesticide Type**	**Crop Use**	**Reason for Exclusion\Inclusion**
2,4-D Triisopropylamine salt	Herbicide (broadleaf)	Commercial turf	not a new a.i.
Famoxadone	Fungicide	Cucurbits, lettuce, peppers, potatoes, tomatoes	Not excluded use >5,000 lbs
Flonicamid	Insecticide	Greenhouse and outdoor ornamentals	Not excluded use >5,000 lbs
Fluroxypyr	Herbicide (broadleaf)	Turf and non-crop area	Use < 5,000 lbs
Fluroxypyr, 1-methylheptyl ester	Herbicide (broadleaf, grasses)	Commercial turf, sod farms, Golf courses	Use < 5,000 lbs
Foramsulfuron	Herbicide (grass)	Turf	Use < 5,000 lbs
Gamma-cyhalothrin	Insecticide	Field grown and row vegetables, alfalfa, tree nuts, stone fruits, tomatoes, wheat	Use < 5,000 lbs
Imazapic, ammonium salt	Herbicide (non-selective)	Turf	Use < 5,000 lbs
Imazapyr	Herbicide (broadleaf)	Non-crop areas	Use < 5,000 lbs (Ag use)
MCPP-P, potassium salt	Herbicide (broadleaf)	Turf	Use < 5,000 lbs
Orthosulfamuron	Herbicide (non-selective)	Rice	Use < 5,000 lbs
Penoxsulam	Herbicide (non-selective)	Rice	Not excluded use >5,000 lbs
Sodium carbonate peroxyhydrate	Fungicide/algicide	Golf course turf	biopesticide
Spiromesifen	Insecticide/miticide	Field grown vegetables, greenhouse ornamentals, landscape ornamentals	Not excluded use >5,000 lbs
Thiacloprid	Insecticide	Pome fruits	Use < 5,000 lbs

Appendix 1. Active ingredients registered by the Department of Pesticide Regulation from 2005 through 2010.

2006			
A.I. Registered	**Pesticide Type**	**Crop Use**	**Reason for Exclusion\Inclusion**
Tralkoyxdim	Herbicide	Barley and wheat	Use < 5,000 lbs
Trifloxysulturon-sodium	Herbicide (non-selective)	Almonds, citrus, cotton, ornamental turf, golf courses, sod farms	Use < 5,000 lbs
Dimethenamid-P	Pre-emergent herbicide	Broadleaf and grassy weeds	Use < 5,000 lbs
Flumiclorac-pentyl	Herbicide (broadleaf)	Corn and soybeans	Use < 5,000 lbs
Imazapic	Herbicide	Broadleaf and grassy weeds	Use < 5,000 lbs
Aminopyralid, triisopropanolamine salt	Herbicide (broadleaf)	Rangeland, pastures, non-cropland	Use < 5,000 lbs
Sulfentrazone	Herbicide (broadleaf)	Lawns, turf areas	Use < 5,000 lbs
Propamocarb hydrochloride	Fungicide	Potatoes	Use < 5,000 lbs
2007			
Chlorhexidine gluconate	Antimicrobial	Hard, non-porous surfaces	Antimicrobial
Copper citrate chelate	Algaecide	Potable water, reservoirs, ponds, canals	Use < 5,000 lbs
Copper gluconate chelate	Algaecide	Potable water, reservoirs, ponds, canals	Use < 5,000 lbs
Cyazofamid	Agricultural fungicide	Cucurbits, potatoes, and tomatoes	Use < 5,000 lbs
Flonicamid	Insecticide	Cotton, potatoes, pome fruit, and stone fruit	Not excluded use >5,000 lbs
Metaflumizone	Insecticide	Fire ants in turf and ornamentals	Use < 5,000 lbs
Potassium silicate	Insecticide, miticide, fungicide	Agricultural crops, ornamentals, turf	Use < 5,000 lbs
Spinetoram	Insecticide	Berries, corn, pome fruit, bulb vegetables, vegetables, tree fruits, ornamentals	Not excluded use >5,000 lbs

Appendix 1. Active ingredients registered by the Department of Pesticide Regulation from 2005 through 2010.

2008			
A.I. Registered	**Pesticide Type**	**Crop Use**	**Reason for Exclusion\Inclusion**
Spirodiclofen	Miticide	Citrus, grapes, pome fruit, stone fruit, and tree nuts	Not excluded use >5,000 lbs
Sulfosulfuron	Herbicide	Wheat, soybeans, potatoes, and turf	Use < 5,000 lbs
Triallate	Herbicide	Wheat	Use < 5,000 lbs
Spirodiclofen	Miticide	Citrus, grapes, pome fruit, stone fruit, and tree nuts	Not excluded use >5,000 lbs
Chlorantraniliprole	Insecticide	Tree fruits, ornamentals, cotton, grapes, potatoes, field crops	Not excluded use >5,000 lbs
Flubendiamide	Insecticide	Eggplant, cucumbers, cabbage, almonds, peaches, cotton	Not excluded use >5,000 lbs
Fluopicolide	Fungicide	Cucumbers, bell peppers, celery	Not excluded use >5,000 lbs
Glyphosate, dimethylamine salt	Herbicide (non-selective)	Agricultural/Industrial	not a new a.i.
Mandipropamid	Fungicide	Leafy vegetables, cucurbits, fruiting vegetables	Not excluded use >5,000 lbs
Orthosulfamuron	Herbicide (broadleaf)	Rice	Use < 5,000 lbs
Paecilomyces lilacinus strain 252	Nematicide	Tree fruits, nuts, leafy vegetables, turf	Biological Use < 5,000 lbs
2009			
Tribenuron-methyl	Herbicide (technical)		Use < 5,000 lbs
Fluoxastrobin	Fungicide	Turf, potatoes, peanuts, tuberous vegetables	Use < 5,000 lbs
Ipconazole	Fungicide	Beets, amaranth, cotton, broccoli, sorghum	Use < 5,000 lbs
Metconazole	Fungicide	Stone fruits, tree nuts, peanuts, turf, ornamentals	Not excluded use >5,000 lbs
Sorbitol octanoate	Insecticide	Fruits, vegetables, Christmas trees	Use < 5,000 lbs
Tetraconazole	Fungicide	Grapes, sugarbeets	Use < 5,000 lbs
Triticonazole	Fungicide	Turf	Use < 5,000 lbs

Appendix 1. Active ingredients registered by the Department of Pesticide Regulation from 2005 through 2010.

2010			
Dicamba, potassium salt	Herbicide	Lawns, turf	Use < 5,000 lbs
Fosthiazate	Nematicide	Tomatoes	Use < 5,000 lbs
Iron HEDTA	Algaecide/Herbicide	Turf	Use < 5,000 lbs
Methyl Iodide	Fumigant (preplant)	Strawberries, vegetables, fruits	Removed from registration
Metrafenone	Fungicide	Grapes	Use < 5,000 lbs
Pinoxaden	Herbicide	Wheat, barley	Use < 5,000 lbs
Saflufenacil	Herbicide	Fruits, nuts	Use < 5,000 lbs